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ZnO MICRORODS SURFACE-DECORATED BY WO_3 NANORODS FOR ENHANCING NH_3 GAS SENSING PERFORMANCE

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ABSTRACT

Regularly shaped, single-crystalline ZnO microrods (MRs) with wurtzite structure were prepared via a wet chemical method. The obtained rods possess average diameter and length of 350 nm and 3.5 µm, respectively. Besides, WO_3 nanorods (NRs) with the size of 20 nm in diameter and 120 nm in length were synthesized by hydrothermal route. A facile solid state reaction route was employed to synthesize the WO_3/ZnO structure by grinding WO_3 NRs powder and ZnO MRs powder with various weight ratios (1:2, 1:1 and 2:1) together at room temperature without any surfactant and template. WO_3 NRs were sprinkled on ZnO MRs surface and it was observed that the amount of WO_3 significantly affected the overall surface of ZnO MRs. Furthermore, NH_3 gas-sensing property of the obtained products were studied and compared with that of sole ZnO MRs sample. The results demonstrated that the sensors based on WO_3/ZnO structures possessed larger response, better selectivity, faster response/recovery than the sensor based on pure ZnO MRs. Especially, the gas sensing property of the WO_3/ZnO composite based sensor with weight ratio of 1:1 was superior to others. However, the operating temperature is quite high (400 °C). The mechanism of gas sensing was also studied.

Keywords: WO_3/ZnO composite, NH_3 gas sensor, hydrothermal treatment.

1. INTRODUCTION

Ammonia is utilized extensively in many chemical industries, fertilizer factories, refrigeration systems, etc. It is harmful and toxic in nature and can result in health hazards such as chronic lung disease, irritating and even burning the respiratory track, etc. It is therefore necessary to develop an ammonia gas sensor to detect and warn the NH_3 leakage in the environment. All industries working with ammonia have an alarm device to monitor NH_3 concentration in several systems such as food technology, chemical engineering, medical diagnosis, environmental protection, and other industrial processes.

Seiyama et al. proposed the gas sensors based on ZnO thin films for the first time [1]. ZnO is sensitive to many gases such as H_2 [2], O_2 [3], H_2O [4], C_2H_5OH [5], NH_3 [6], etc. Some

disadvantages such as high operating temperature, poor gas selectivity and low gas sensitivity are challenges for real applications. ZnO(n)/CuO(p) heterocontact configuration showed highly sensitive and selective toward H_2S [7]. D. Yang et al. improved the NH_3 gas selectivity and sensitivity of the ZnO nanoparticles by doping with α-Fe_2O_3 nanoparticles [8]. The porous flower-like CuO/ZnO nanostructures exhibited a higher response and lower working temperature with certain organic vapors, such as ethanol, acetone, and formaldehyde, comparing with pure ZnO [9]. A Fe_2O_3 mixed with ZnO thick film was observed to be highly sensitive to ammonia gas at 350 °C and no cross response to other hazardous and polluting gases such as LPG, CO_2, C_2H_5OH, H_2 and Cl_2 [10]. The sensor based on ZnO/α-Fe_2O_3 hierarchical nanostructures exhibited a much higher sensitivity to ethanol vapor than pure ZnO [11]. A WO_3/ZnO thin – film heterojunction exhibited faster response and recovery towards hydrogen [12]. Li et al. have prepared flower-like ZnO bunches by a direct precipitation method [13]. Sow et al. have synthesized ZnO-CuO nanostructure by directly heating a CuZn alloy (brass) on a hotplate in ambient conditions [14]. CuO-ZnO composite hollow spheres were prepared by one-pot, glucose-mediated hydrothermal reaction with subsequent heat treatment [7]. Wei et al. have successfully prepared WO_3-ZnO composites via an aqueous solution route at low temperature [15]. Mohamed et al. have synthesized ZnO nanorods surface-decorated by WO_3 nanoparticles by combining a hydrothermal technique with a chemical solution process [16].

In this work, we study and compare the ammonia sensing properties of WO_3 nanorods (NRs)/ZnO microrods (MRs) composite configuration. Herein, ZnO MRs surface-decorated by WO_3 NRs were synthesized using a template-free and economical hydrothermal method combined with subsequent calcination. The obtained nanomaterials were analyzed by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). Experimental results showed that a WO_3/ZnO heterostructure exhibits excellent gas sensing signals towards NH_3 that elucidate the superior sensing properties of the WO_3/ZnO with faster response and higher sensitivity than sole ZnO MRs-based sensor.

2. EXPERIMENTAL

WO_3 NRs were synthesized by hydrothermal method with sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) as precursor and distilled water as solvent. In a typical experiment, 4.125 g $Na_2WO_4.2H_2O$ was dissolved into 12.5 ml of distilled water and stirred for 30 minutes to form a translucent 1 M Na_2WO_4 solution. Then, 3 M HCl solution was subsequently dropped during stirring in succession to acidify the Na_2WO_4 solution to a pH of 1.8. The mixed reaction system was stirred for 4 h to become a homogeneous and stable solution. The prepared solution was then transferred to and sealed in a 20 ml teflon-lined stainless steel autoclave and the temperature was set at 120 °C for 24 h under autogenous pressure. The pH of the solution remained 2 during the whole synthesis process. After that, the autoclave was cooled naturally to room temperature. The obtained powder was washed several times with distilled water and ethanol to remove ions possibly residues, and then dried at 80 °C for 24 h in air.

The synthesis of ZnO MRs was conducted as follows: All reagents were analytically pure and used without further purification after purchase. In a typical procedure, zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ (99 %) (7.512 g) was dissolved in 50 ml distilled water under gently magnetic stirring for 15 minutes to obtain 0.5 M $Zn(NO_3)_2$ solution. Also, potassium hydroxide KOH (85 %) (19.8 g) was dispersed in 200 ml distilled water and mildly stirred for 5 minutes to prepare 1.5 M KOH solution. After that, 83 ml 1.5 M KOH solution was slowly dropped into the 0.5 M $Zn(NO_3)_2$ solution with a speed of 3 ml/min and the mixture was stirred

continually for 15 min at room temperature. Then, the mixture was transferred into a 20 ml teflon-lined stainless steel autoclave and put inside an electric oven at 180 °C for 48 h under autogenous pressure. After being cooled down to room temperature naturally, the white precipitate (zinc hydroxide $Zn(OH)_2$) was collected, washed by filtering several times with distilled water and absolute ethanol (99.6%), and subsequently dried at 80 °C for 24 h.

To obtain WO_3/ZnO composite structure, 0.04 g of WO_3 NRs powder and 0.04 g of ZnO MRs powder were weighed and dispersed in 0.4 ml distilled water. WO_3 NRs and ZnO MRs slurries were blended together (in weight ratio of 1:2, 1:1 and 2:1) in an agate mortar and ground thoroughly for 20 min at room temperature.

The phase crystalline structure of the as-synthesized nanocrystals were examined by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer, using Cu-K_α radiation with a wavelength of 1.5406 Å over a scanning angle 2θ range from 20° to 70°. The morphology and the elemental analysis of the obtained samples were investigated using field emission scanning electron microscopy (FESEM) on a Hitachi S4800 or Quanta JSM 6301F, operating at 10 kV and energy dispersive X-ray spectroscopy (EDS, OXFORD JEOL 5410 LV) operating at 15 kV.

As-prepared porous rod-like WO_3/ZnO structure and ZnO MRs were directly coated on the surface of a Si/SiO_2 substrate attaching a pair of Pt interdigitated electrodes, then drying at 80 °C in air for 24 h, subsequently annealing at 400 °C for 2 h. An external source provided the working temperature of the gas sensor through the sample holder. To improve the long-term stability, the sensors were kept at the working temperatures for 2h before measuring gas sensing characteristics. A stationary state gas distribution method was used for testing gas response in air. In measuring the voltage, a load resistor was connected in series with the gas sensors. The circuit voltage was set at 5 V and the output voltage was the terminal voltage of the load resistor. The test was performed in a static measuring system. Detected gases (NH_3, C_2H_5OH, CH_3COCH_3, LPG) were injected into a test chamber and mixed with air. The gas response of the sensor was defined as $S=R_a/R_g$ (reductive gas), where R_a is the resistance in air and R_g reflects the resistance in the air mixed with detected gas. The response or recovery time was expressed as the time acquired for the sensor output to reach 90% of its saturation value after applying or switching off the gas in a step function.

3. RESULTS AND DISCUSSION

3.1. Structural characterization of WO_3/ZnO composites

The crystalline phase of the ZnO precursor is shown in Fig. 1a. All the diffraction peaks can be indexed as hexagonal wurtzite structure in accordance with JCPDS card number 79-0205 for ZnO. Fig. 1b shows the XRD pattern of WO_3 NRs. All the diffraction peaks of pre-annealed WO_3 can be indexed to hexagonal structure WO_3 (h-WO_3) (JCDPS card number 75-2187). From Fig. 1c, the characteristic peaks of hexagonal wurtzite ZnO and hexagonal structure WO_3 (h-WO_3) were observed. Novel peaks were not observed in the XRD pattern of the WO_3/ZnO sample, hence, no new crystallized structure was obtained.

3.2. Morphology of obtained WO_3/ZnO composites

The morphology of the WO_3 NRs, ZnO MRs and WO_3/ZnO composite was characterized by FESEM and illustrated in Fig. 2 (a, b, c), respectively. The WO_3 NRs have widths of ~20 nm

and lengths of ~120 nm. The maximum length approximates 200 nm and maximum width ~25 nm. At low magnification (Fig. 2b), the as-prepared ZnO powder sample consists of relatively uniform and smooth surface rod-like micro-structures with length of 3.5 μm and hexagonal cross section with diameter of 350 nm. Figure 2c illustrated that most of the products have maintained the rod-shape of the precursor without significant change after blending with WO_3 NRs. However, a large amount of irregular WO_3 bundles of hundreds of nanometers were randomly distributed and covered on the ZnO MRs surface, which made them becoming rougher. Giant rods of ZnO species associated with smaller nanorods of WO_3 show more porosity, giving larger effective surface area, which enables larger surface for the gas to react and gives higher response.

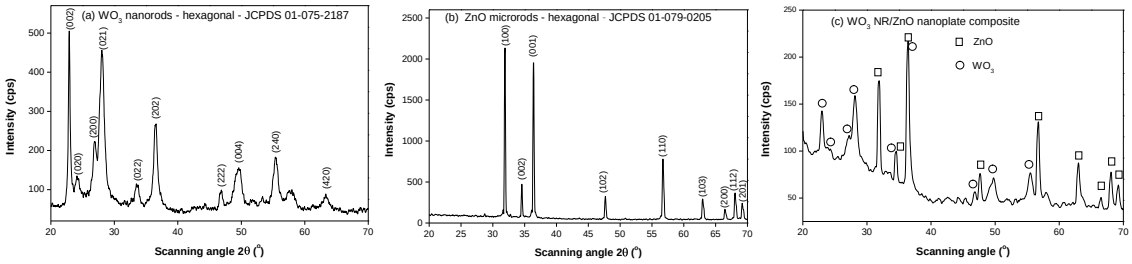


Figure 1. XRD patterns of WO_3 nanorods (a), ZnO microrods (b) and WO_3/ZnO composite (c).

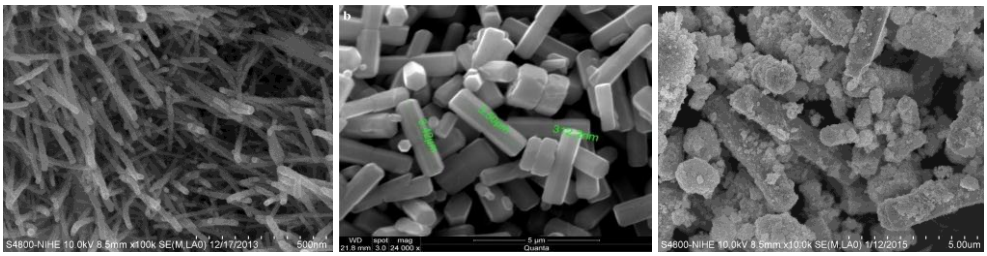
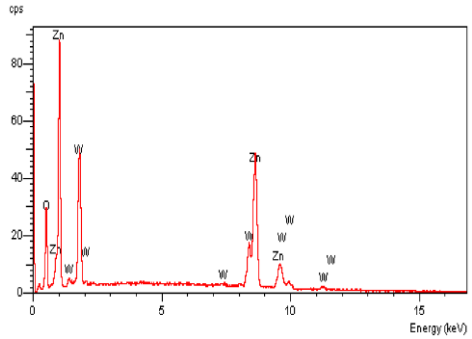


Figure 2. FESEM images of (a) pure WO_3 NRs, (b) sole ZnO MRs and (c) WO_3/ZnO composite.



WO_3/ZnO	2:1		1:1		1:2	
Element	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
O	20.37	64.57	20.21	60.3	20.1	56.5
Zn	26.75	20.87	40.12	29.4	53.5	37.1
W	53	14.57	39.65	10.3	26.43	6.47
Total	100	100	100	100	100	100

Figure 3. EDS pattern and composition table of WO_3/ZnO composite.

3.3. Compositional characterization

Result from EDS analysis (Fig. 3) reveals that the products are formed by Zn, W and O elements. It was calculated that the composition results were almost consistent with the weight ratios of WO_3 and ZnO which approximate the designed compositions.

3.4. Gas sensing characterization

The sensor film was initially tested for the detection of NH_3 in air in order to optimize acquisition parameters. Fig. 4 illustrates the typical response-recovery characteristics of the gas sensor based on WO_3/ZnO composite thin film to ammonia gas with concentrations of 25 – 300 ppm at different working temperatures. It was found that the resistance of the material decreased with the temperature increase, thus the observation is consistent with the semiconducting behavior of the metal oxide material. WO_3 and ZnO are both n-type semiconductor, so the resistance of WO_3/ZnO composite decreased when the sensor was exposed to NH_3 gas (a reducing gas) and the material responded almost instantaneously to the change of air to NH_3 gas. It is generally accepted that the electrical conductivity of WO_3 depends critically on its stoichiometry and particularly the presence of oxygen vacancies in WO_3. Electrical conductivity increases at higher defect concentration [17]. Considering the sensitivity of gas sensor is greatly influenced by operating temperature, parallel experiments were carried out in the range of 250–400 °C to optimize the proper operating temperature of the sensor. As can be seen, the sensor exhibits both excellent sensitivity and good reproducibility when exposed to various ammonia concentrations. The response could be attributed to the adsorption-desorption type sensing mechanism. Gas sensing mechanism is explained in term of resistance by adsorption of atmospheric oxygen on the surface and direct reaction of adsorbed oxygen ions with the test gas. The giant rods of ZnO and smaller rods of WO_3 form the large intergranular potential barrier. When ammonia reacts with adsorbed oxygen on the surface of the film, it gets oxidized to nitrogen oxide gas and liberates free electrons back to the conduction band. The generated electrons contribute to an increasing carrier concentration of the sample, which results in a thin space-charge layer and decreases the potential barrier, thereby decreasing resistance of the film [10]. Moreover, when WO_3/ZnO sensor is exposed to NH_3, more trapped electrons are released due to different band gaps (WO_3: 2.7 eV, ZnO: 3.37 eV) and electron affinities (WO_3: 4.92 eV, ZnO: 4.05 eV), which results in a thinner space-charge layer and further decreases the potential barrier [11].

The response to NH_3 of WO_3/ZnO composites as a function of ammonia concentration at different temperatures is shown in Fig. 4 (b, d, f). The sensor response increases with the concentration of ammonia gas. Fig. 4g shows the response to 300 ppm NH_3 as a function of operating temperature. A sensitivity of WO_3 NR/ZnO MR=1:1 in weight to 300 ppm NH_3 as high as 26 can be obtained at 400 °C as compared to 3.65 of sole ZnO MRs sample (7 times higher in response). There was apparent change in response time (from 100 s to 30 s) or rate of response (the time required to reach steady condition). Although the sensitivity and rate of response were improved significantly, the optimum working temperature increased from 300 °C to 400 °C is the main disadvantage of this sample. Fig. 4e shows the selectivity of the gas sensor based on WO_3 NRs/ZnO MRs composite with composition of 1:1 in weight. The sensor was exposed to ammonia (NH_3), ethanol (C_2H_5OH), acetone (CH_3COCH_3), LPG (liquefied petroleum gas) of the same concentration level of 300 ppm at 400 °C. It is clear that the response to NH_3 is fairly high (about 26), whereas that to other gases is much lower (the response to ethanol, acetone, LPG are 2, 5, 5, respectively). This sensor exhibits the largest response to NH_3, among all the tested gases.

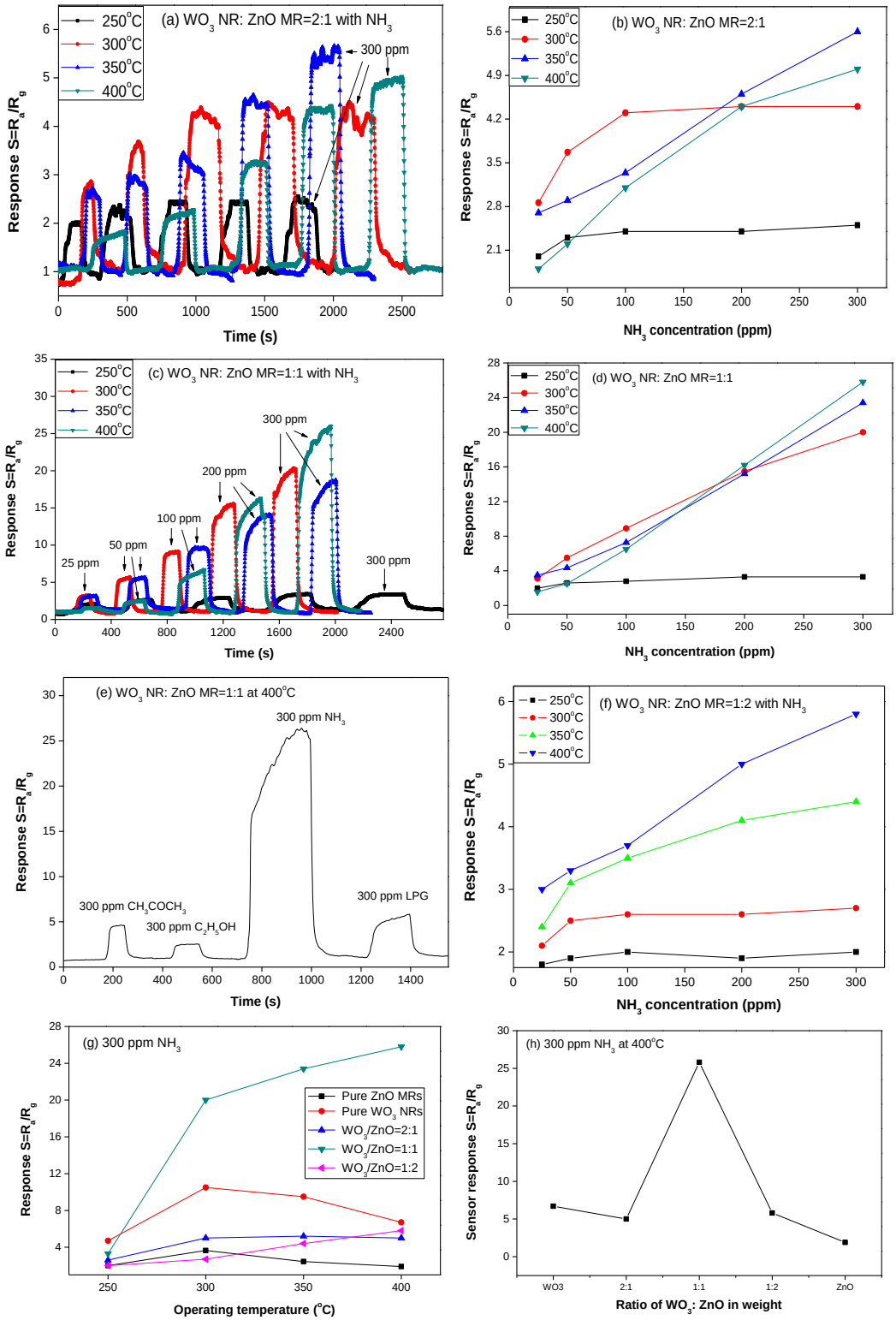


Figure 4. Gas sensing properties of WO_3/ZnO composite.

Table 1. NH_3 sensing parameters of WO_3/ZnO composite.

Ratio	T_o	S	τ_{res}	τ_{rec}
WO_3	300°C	10.5	110 s	40 s
ZnO	300°C	3.65	100 s	55 s
2:1	350°C	5.2	50 s	75 s
1:1	400°C	25.8	30 s	110 s
1:2	400°C	5.8	60 s	140 s

T_o optimum working temperature, S sensor signal $S = R_a/R_g$, τ_{res} response time, τ_{rec} recovery time

These results indicate the fairly good NH_3 sensitivity and selectivity of the WO_3/ZnO (1:1 in weight) composite thin film compared to other samples. The sensitivity towards NH_3 is significantly improved as blending WO_3 NRs with ZnO MRs compared to pure materials. An interesting phenomenon is noticed in Fig. 4f that the response of WO_3/ZnO=1:2 in weight based sensor is the lowest compared with that of the others, except the pure ZnO sensor. From the SEM image (Fig. 2), it can be seen that the size of ZnO microrods is larger than that of the WO_3 nanorods. The result indicated that the large ZnO rods is adverse to the gas sensitivity of sensor. Table 1 summarizes the sensor signal (response magnitude), response time and recovery time of the sensors based on pure WO_3 NRs, sole ZnO MRs, WO_3/ZnO composites with different weight ratios (2:1, 1:1, 1:2). The gas sensitivity of the sensor based on WO_3: ZnO=1:1 is highest with the shortest response time ca. 30 s compared to other compositions. It can be concluded that WO_3: ZnO=1:1 presents a maximum of response during gas test at 400 °C (Fig. 4h).

4. CONCLUSIONS

In summary, WO_3/ZnO composites were synthesized by a facile hydrothermal reaction route and blended together in weight ratio of 2:1, 1:1 and 1:2 without using any surfactant and template at room temperature. FESEM images showed that added WO_3 NRs affect profoundly on morphology of ZnO microrods from smooth to rough surface. The gas-sensing measurements demonstrated that the sensor based on WO_3/ZnO composite exhibited a higher sensitivity, better selectivity and reproducibility to ammonia gas than the sensor based on sole ZnO microrods. The optimum performance was obtained at 400 °C for the WO_3 NRs sensor blended with 50 wt.% ZnO MRs. The composite sensors also presented rapid response characteristics because of the large surface-to-volume ratio of WO_3/ZnO composite. Although further studies to reduce the operating temperature and recovery time of the composite are necessary, WO_3/ZnO composite with the ratio of 1:1 in weight is believed as a potential candidate to fabricate ammonia sensor.

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TÓM TẮT

BỀ MẶT THANH MICRO ZnO ĐƯỢC BAO PHỦ BỞI THANH NANO WO_3 NHẰM TĂNG CƯỜNG ĐẶC TÍNH NHẠY KHÍ NH_3

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Thanh micro ZnO đơn tinh thể, hình dạng đồng đều, cấu trúc wurtzite được chế tạo bằng phương pháp thủy nhiệt có đường kính 350 nm và chiều dài 3.5 μm. Thanh nano WO_3 có đường kính 20 nm và chiều dài khoảng 120 nm cũng được chế tạo bằng phương pháp thủy nhiệt. Cấu trúc tổ hợp WO_3/ZnO được chế tạo bằng phương pháp phản ứng pha rắn với các tỉ số khối lượng 1:2, 1:1 và 2:1 không sử dụng khuôn hay chất hoạt động bề mặt. Thanh nano WO_3 bám trên bề mặt thanh ZnO không làm thay đổi hình dạng thanh ZnO. Tính chất nhạy khí NH_3 của vật liệu tổ hợp được so sánh với thanh micro ZnO thuần. Kết quả cho thấy tính chất nhạy khí được cải thiện đáng kể, độ đáp ứng cao hơn, khả năng chọn lọc khí tốt hơn, nhiệt độ làm việc thấp hơn, tốc độ đáp ứng nhanh hơn so với thanh micro ZnO thuần. Tỉ số khối lượng 1:1 giữa WO_3 và ZnO là tối ưu so với các tỉ lệ khác. Tuy nhiên, nhiệt độ làm việc khá cao (400 °C). Cơ chế nhạy khí cũng được thảo luận.

Từ khóa: tổ hợp WO_3/ZnO, cảm biến khí NH_3, xử lý thủy nhiệt.